Micellar Morphology in Bulk Styrene-Core Ionic Diblock Copolymers

Diep Nguyen,[†] Sunil K. Varshney,[†] Claudine E. Williams,[‡] and Adi Eisenberg*,[†]

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6, and Laboratoire pour l'Utilisation du Rayonnement Électromagnétique (LURE), CNRS-CEA-MEN, Université Paris-Sud, 91405 Orsay Cedex, France

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ABSTRACT: Diblock ionomers consisting of a short polystyrene block and a long ionic segment of poly(4-vinylpyridinium methyl iodide) or poly(cesium methacrylate) have been investigated by small-angle X-ray scattering in the solid state. The size of the spherical microdomains formed by the polystyrene blocks in the continuous ionic matrix has been measured and compared to that of the mirror system consisting of an ionic core in a nonionic matrix, previously investigated. Similar chain stretching of the core-forming block is observed for both systems, and it is concluded that the chain extension in the microdomains is due to the high surface energy between the ionic and the nonionic phases rather than to specific ionic interactions. In addition, the core radii of the two mirror systems were fitted to the predictions of the star model for block copolymers, $R \propto aN_B^{3/5}$, where N_B is the length of the core-forming block.

Introduction

Microphase separation is a common feature of most block copolymers because of the incompatibility between the different segments. In block ionomers, i.e., block copolymers in which one of the moieties contains charged groups, the dipolar attraction between the ionic blocks in an apolar medium further enhances phase separation. Furthermore, since the ion content is kept low in ionomers, usually at less than 20 mol %, the ionic blocks of AB and ABA block ionomers are short and self-assemble into spherical microdomains dispersed in the nonionic matrix. The assemblies can be described as inverted micelles, by analogy to the reverse micelles formed by low molecular weight surfactants. Previous structural studies by small-angle X-ray scattering (SAXS),[1-3] small-angle neutron scattering (SANS),[4] and transmission electron microscopy (TEM)[5] of polystyrene-based block ionomers in the dry state have shown that the short ionic blocks are highly extended in their spherical microdomains[1-4] whereas the polystyrene blocks are not affected by the strong binding of their chain ends and, on average, keep a Gaussian configuration.[4] It was suggested that the extension, which minimizes the total interfacial area, is due to the high surface energy difference between the two highly incompatible blocks rather than to the ionic character of the micellar core.

To ascertain experimentally whether this hypothesis is correct, one should use a mirror system to the one described above, i.e., one consisting of spherical nonionic microdomains dispersed in an ionic matrix and, most importantly, which has the same interfacial energy. For this purpose, diblock ionomers with a short nonionic segment of polystyrene and a long ionic one of poly(4-vinylpyridinium iodide) or poly(cesium methacrylate) have been investigated by SAXS. We show in this report that the short nonionic (polystyrene) segments are also highly extended in their microdomains.

Experimental Section

1. **Reagents and Solvents.** Styrene and α-methylstyrene (Aldrich) were dried over CaH_2 for 24 h, distilled under vacuum, and stored under nitrogen at −20 °C. They were then treated with fluorenyllithium for 15 min and distilled under vacuum just prior to the polymerization. 4-Vinylpyridine (Aldrich) was dried over CaH_2 for 24 h, distilled under vacuum, and stored under nitrogen at −20 °C. It was treated with a mirror of sodium under nitrogen (a light yellow color developed) and distilled under vacuum just before the polymerization. *tert*-Butyl methacrylate (tBuMA) (Polysciences) was also dried over CaH_2 for 24 h, vacuum distilled, and stored under nitrogen in the dark at −20 °C. It was treated with a 10 wt % triethylaluminum solution in hexanes at 0 °C until a persistent greenish-yellow color was observed.[6] It was finally distilled under vacuum prior to polymerization. Tetrahydrofuran (THF) was purified by refluxing over a sodium-benzophenone complex under dry nitrogen, a blue-violet color indicating a solvent free of oxygen and moisture.

The initiator used to prepare poly(styrene-*b*-*tert*-butyl methacrylate) (PS-*b*-PtBuMA) and poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer was the reaction product of *sec*-butyllithium with a few units of α-methylstyrene[7] in THF. It was prepared in the glass reactor which was also used for the polymerization. A deep red solution was developed at room temperature.

2. **Polymerization.** The anionic block copolymerization of styrene and tBuMA or 4VP was carried out under a nitrogen atmosphere in a preflamed glass reactor, the monomers, solvents, and initiator being transferred by syringe and capillary techniques. Block copolymerization was carried out in THF at −78 °C. Styrene was added dropwise, with vigorous stirring, by means of a capillary. The dark red color of the initiator solution changed quickly to a deep orange-yellow color. After a few minutes, the color of the solution turned back to red, indicating the completion of styrene polymerization. An aliquot of the solution was withdrawn for analysis by size exclusion chromatography (SEC) to determine the chain length of the polystyrene block. tBuMA or 4VP was then added to the polymerization medium. Upon addition of a few drops of the tBuMA or 4VP, the red color of the living poly(styryllithium) anions changed instantaneously to a light yellow color for tBuMA anions or a deep orange-yellow color for 4VP anions. After 15 min the reaction was terminated with methanol. The polymer was recovered by precipitation in hexanes and dried in a vacuum oven at 80 °C for 48 h.

3. **Polymer Characterization.** Size exclusion chromatography (SEC) was performed with a Varian 5010 liquid chromatography unit equipped with four columns of 10^4, 10^3, 500, and 100 Å (Shoko Ultrastyragel) with THF as the eluent at a flow rate of 1 mL/min at 30 °C. Standard polystyrenes were used to

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* To whom correspondence should be addressed.

[†] Department of Chemistry, McGill University.

[‡] LURE, CNRS-CEA-MEN, Université Paris-Sud.

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Table 1. Relevant Parameters for the Systems[a]

		parameters calcd from SAXS				
samples	M_w/M_n	R_{shape} (Å)[d]	R_{SC} (Å)[e]	R_{BCC} (Å)[e]	R_{FCC} (Å)[e]	R_{HCP} (Å)[e]
PS-*b*-PtBuMA[b]						
24-*b*-80	1.20	50	50	56	54	43
24-*b*-165	1.30	50	52	58	56	45
40-*b*-150	1.30	(45)	60	69	67	54
PS-*b*-P4VP[c]						
19-*b*-95			50	54	53	42

[a] Polystyrene blocks have $M_w/M_n = 1.10$. [b] Value determined by SEC. [c] Value determined by proton NMR. [d] R_{shape} values were deduced from shape factor peaks. [e] Values of R were deduced from space-filling calculations.

calibrate the instrument, and the number-average molecular weights of the polystyrene and block copolymers with poly(*tert*-butyl methacrylate) (PtBuMA) were calculated using Varian DS-604 computer software. As the block copolymer of PS-*b*-P4VP was not eluted in these columns in THF at 30 °C, the composition of this block copolymer was determined by proton NMR. The relevant parameters of these diblocks are presented in Table 1.

4. Hydrolysis. PS-*b*-PtBuMA block copolymers were hydrolyzed to polystyrene-*b*-poly(methacrylic acid) (PS-b-PMAA) using *p*-toluenesulfonic acid (PTSA) as a catalyst.[8] The polymer was recovered and purified by repeated precipitations into cold methanol. It was then vacuum dried at 50 °C for 48 h.

5. Neutralization.

The dried PS-*b*-PMAA block copolymers were neutralized in benzene/methanol (50:50 v/v) with a stoichiometric amount of CsOH. The methanol was removed under vacuum and the ionomers were recovered by freeze-drying. The samples were further vacuum dried at 60 °C for 72 h.

6. Quaternization. Quaternization of samples of PS-*b*-P4VP diblock copolymers with CH_3I was performed in THF at room temperature using a procedure similar to that described by Arai *et al.*[9]

The abbreviations used to indicate the copolymer composition are as follows: PS(19)-*b*-P4VP(95) means a polystyrene chain of 19 units joined to a poly(4-vinylpyridine) chain of 95 units. The quaternized form is denoted by the extension MeI. Similarly, PS(25)-*b*-PMA Cs (165) indicates a polystyrene chain of 25 units joined to a poly(methacrylic acid) chain of 165 units neutralized with Cs.

7. Samples for SAXS. The neutralized PS-*b*-PMACs samples were dissolved (10 wt %) in a THF/methanol (70:30 v/v) solvent mixture. The quaternized PS-*b*-P4VPMeI copolymer was dissolved (10 wt %) in a DMF/water (95:5 v/v) solvent mixture. Slow evaporation of the solvents over a period of 48 h at room temperature yielded brittle films that were further vacuum dried at 60 °C for 48 h prior to SAXS investigation.

8. SAXS Instrumentation. The small-angle X-ray scattering experiments were performed at the D22 station[10,11] of the LURE–DCI synchrotron radiation source (Orsay, France). The double-crystal, fixed-exit monochromator was tuned to provide a beam of 9 keV, collimated to about 1 mm² at the sample. The beam path, including the sample holder, was kept under vacuum. The scattered X-rays were detected with a Xe–CO_2 gas filled, one-dimensional position-sensitive detector with a spatial resolution of 257 μm. All the samples were studied in the angular q range from 0.006 to 0.30 $Å^{-1}$ ($q = 4\pi \sin \theta/\lambda$, where θ is half the scattering angle and λ is the X-ray wavelength). The resulting intensity (I) vs q curves were corrected for beam decay, sample absorption, and sample thickness; a background scattering from a polystyrene homopolymer or from the empty sample holder was subtracted.

Results and Discussion

A sharp asymmetric peak followed by a weaker broad halo at higher q was observed for all PS-*b*-PMACs samples; for the PS-*b*-P4VPMeI sample, only a broad asymmetric peak was seen. Figure 1 presents the SAXS profile of the sample PS(24)-*b*-PMACs(165); for comparison, the profile of the "mirror" system of this sample,[5] i.e., PS(166)-*b*-PMACs(25), is also shown as an insert. The scattering pattern of the nonionic core system has the same general features as that of the ionic core system. The only difference observed here was that the peak at high q is broader and less intense. Because of the similarities, the SAXS data have been analyzed in the same way as was used for the inverse micelle system.[1,2] Here also a spherical morphology has been assumed for the nonionic domains, justified by the low volume fraction of the polystyrene phase (<13% in this case). Note that for the mirror system, the presence of spherical ionic microdomains has been well documented[1,2] and further confirmed by transmission electron microscopy (TEM).[5] Here the volume fraction of each block is such that the continuous phase is P4VPMeI or PMACs while the core is the nonionic polystyrene.

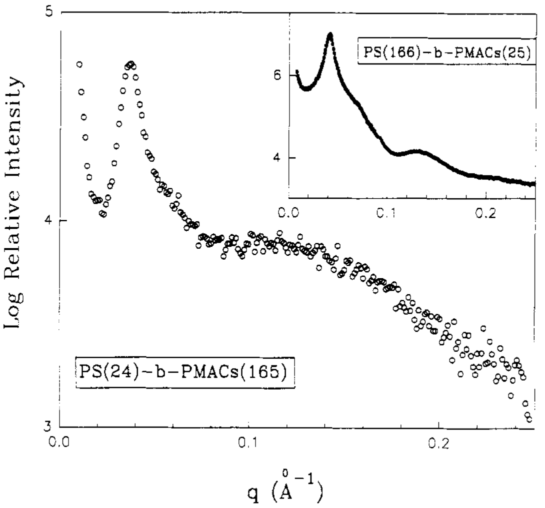

Figure 1. SAXS profile of PS(24)-*b*-PMACs(165). The insert shows the mirror system of PS(166)-*b*-PMACs(25).

The first peak is attributed to an interparticle correlation while the second one, at higher q, is the shape factor for polydisperse spheres. The SAXS data analysis is based on the assumption that the system is completely microphase separated and that the interphase thickness is negligible. This assumption is reasonable in view of the high driving force for the phase separation between the ionic and the nonionic segments, as was also observed for the reverse micelle systems[1-3] that have the same ionic and nonionic segments (P4VPMeI or PMACs and PS) and therefore the same interaction parameters χ. As for the mirror system, the radius of the microdomains has been estimated by two independent methods. First, the position of the shape factor peak provides a direct measurement of the radius, R, of the microdomains since its minima occur at $qR = 4.5$ and 7.7 for $i = 1$ and 2.[13,14] Polydispersity in the sizes of the spheres smears out the minima of the scattering curve until the profile appears smooth for polydispersities larger than 1.1. Such is the case for the PS-*b*-P4VPMeI samples. In principle, one can fit the shape factor peak to the theoretical curve for scattering from spherical objects, assuming a certain distribution in the domain sizes. Here, only the position of the first minimum is visible and only it was used to derive the radius. The complete fit of the shape factor was not meaningful because of the poor signal-to-noise ratio. The second method is indirect and relies on space-filling arguments. Bragg's law has been boldly applied to the position of the first maximum to deduce a characteristic distance, d_B. Knowing the Bragg distance and the volume fraction of the polystyrene phase, it is possible, by using space-filling calculations, to compute a radius of the

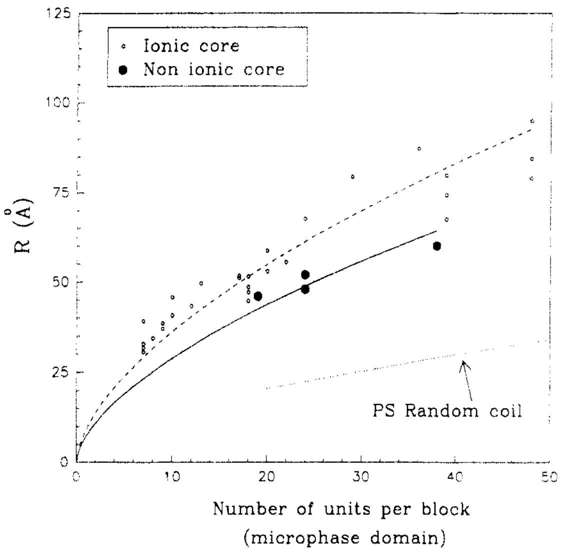

Figure 2. Graph of experimental radius vs number of units per block (microphase domain). The values of the radii of the ionic core are from ref 2. The solid and dashed curves correspond to a fit of the experimental points to Halperin's model.[19]

spherical microdomains assuming that they are arranged on simple cubic, body centered cubic, face centered cubic, or hexagonal close packed lattices.[12] The values of R calculated by both methods are given in Table 1. It should be noted that the best agreement (within 10%) between the sizes calculated by both methods is obtained for spheres arranged on a simple cubic lattice. For the sample PS(40)-*b*-PMACs(150), where the shape factor peak is not well defined, the agreement is poorer, with a difference of 20%. For the PS-*b*-P4VPMeI sample, no shape factor peak was observed. Hence, the values derived for the simple cubic lattice have been considered, only because they provide the best agreement with the shape factor values. The same conclusion concerning the lattice symmetry was reached for the reverse system.[2] However, it should be kept in mind that the strict application of Bragg's law for such a distorted lattice is limited. In the absence of higher order peaks, other types of order (e.g., liquid and amorphous) are also a possibility.

A summary representation of the variation of the radius of the spherical microdomains with the number of units per block, N, in each microdomain is given in Figure 2. For comparison, the values of the radii of the ionic cores[2] for a number of different systems are also included. It can be seen that the radius of the nonionic core is strongly dependent on the number of units in the blocks which make up the phase-separated microdomains. This is in agreement with our previous experimental conclusions for the case of ionic core micelles and with an independent study of Wilkes *et al.*[3] Figure 2 also shows the random coil end-to-end dimension for PS[15] segments, r, which was calculated using the relation $r = (C_\infty N l^2)^{1/2}$, where $C_\infty = 9.5$, $l = 1.54$ Å, and N is the number of C–C bonds. The random coil dimensions have been calculated for segment lengths of 25 units or more. It is noted that the radius of the microdomains is of the same order as the extended length of the block. For instance, for N of 20 units, the fully stretched planar zigzag length, obtained by multiplying the number of units of the core forming block by 2.5 Å, is 50 Å compared to the experimental radius of 50 Å. This was also observed for the ionic core.[1,2] High extension of the segment has also been found theoretically for copolymers in the "superstrong segregation" limit,[16] i.e., when χ is very large; however, this model predicts a linear variation of R with N, for all N, which does not seem to be obeyed in the full range of block lengths investigated here.

The parallel behavior of these two systems, i.e., ionic spheres in a nonionic matrix and nonionic spheres in an ionic matrix, shows that the high extension of the short chains in their microdomains is not due to specific interactions in the core but, more likely, to the high incompatibility between the two polymers. Indeed, because of the high surface energy between the ionic and nonionic phases, the system would tend to maximize the sizes of the microdomain spheres to minimize their total surface area as well as their number. The shorter the chains, the less energy is required to stretch them. With increasing chain length, the energy requirement for complete extension increases exponentially.[17] Therefore, with increasing chain length of the core materials, the energy balance will be less favorable to chain extension.

In a parallel SAXS investigation of the solution properties of AB diblock ionomers with short ionic segments and long PS blocks in toluene, which is a selectively good solvent for the polystyrene blocks, it was found that the sizes of the ionic cores of the samples in solution were the same as those in the solid state when cast from the same solvent.[18] Furthermore, the radii of the ionic microdomains, in solutions, were found to scale with the number of units in the ionic blocks, N_B, as $N_B^{3/5}$, in agreement with Halperin's model for block copolymer micelles in a selective solvent.[19] In this starlike model, the equilibrium structure is determined by the balance of the surface energy of the core, the stretching penalty of the core blocks and of the swollen corona blocks.[20]

Because of the similarities mentioned above between solutions and cast samples, the data for ionic core samples from ref 2 and these data for the PS core have been fitted with the same scaling law. As seen in Figure 2, the agreement is quite satisfactory. The prefactor a, which is probably related to the molecular characteristics of the polymers, is found to be 9.1 for both ionic systems and 7.2 for the nonionic system. The values seem reasonable in views of the differences in the monomer volumes, 255 Å^3/molecule for P4VPMeI, 210 Å^3/molecule for PMACs, and 160 Å^3/molecule for PS.

Conclusions

Nonionic core micelles in an ionic matrix have been obtained with diblock ionomers of short polystyrene chain lengths and long ionic block lengths. Their morphology in the solid state, as studied by SAXS, has been compared to that of the "mirror" system consisting of ionic core in a nonionic matrix. It was found that the short polystyrene blocks in the core are highly stretched, as was the case for the ionic chains in the ionic core systems. Thus, it is concluded that it is the high surface energy rather than the ionic character that drives the chain extension. It was also found that the radii of the microdomains scale as $N_B^{3/5}$ (N_B is the length of the core-forming block) as predicted by the star model for block copolymers.

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References and Notes

(1) Gouin, J. P.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1989**, *22*, 4573.

(2) Gouin, J. P.; Bossé, F.; Nguyen, D.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7250.

(3) Venkateshwaran, L. N.; York, G. A.; DePorter, C. D.; McGrath, J. E.; Wilkes, G. L. *Polymer* **1992**, *33* (11), 2277.

(4) Gouin, J. P.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1992**, *25*, 1368.

(5) Nguyen, D.; Zhong, X. F.; Williams, C. E.; Eisenberg, A. Submitted for publication in *Macromolecules*.

(6) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15*, 127.

(7) Teyssie, Ph.; Jerome, R.; Ouhadi, T.; Fayt, R. U.S. Patent 4,461,874, July 4, 1984.

(8) Long, T. E.; Kinstel, J. F., Eds. *ACS Symp. Ser. 364* **1988**, Chapter 19.

(9) Schwab, F. C. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 435.

(10) Dubuisson, J. M.; Dauvergne, J. M.; Depautex, C.; Vachette, P.; Williams, C. E. *Nucl. Intrum. Methods Phys. Res.* **1986**, *A246*, 636.

(11) Storey, R. F.; George, S. E. *Polym. Mater. Sci. Eng.* **1988**, *58*, 985.

(12) The mass densities of PS, P4VPMeI, and PMACs were taken as 1.05, 1.6, and 1.7 g/mL, respectively.

(13) Hashimoto, T.; Nagatoshi, K.; Todo, A.; Hasegawa, H.; Kawai, H. *Macromolecules* **1974**, *7*, 364.

(14) Guinier, A.; Fournet, G. *Small Angle Scattering of X-rays*; Wiley: New York, 1955.

(15) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley and Sons: New York, 1989.

(16) Nyrkova, I. A.; Khokhlov, A. R.; Doi, M. *Macromolecules* **1993**, *26*, 3601.

(17) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1967.

(18) Nguyen, D.; Williams, C. E.; Eisenberg, A. Submitted for publication in *Macromolecules*.

(19) Halperin, A. *Macromolecules* **1987**, *20*, 2943.

(20) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531.